LA-UR -80-586

TITLE: A NEW IMPROVED STANDARD FOR ELECTRON PROBE DETERMINATION OF ORGANIC SULFUR IN FOSSIL FUELS

AUTHOR(S): L. A. Harris, R. Raymond, and R. Gooley

MASTER

SUBMITTED TO: Microprobe Analytical Society

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

Form No. 836 R3
St. No. 2629
12/78

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

A NEW IMPROVED STANDARD FOR ELECTRON PROBE DETERMINATION OF ORGANIC SULFUR IN FOSSIL FUELS

L. A. Harris, R. Raymond, Jr., and R. Gooley

Electron probe microanalysis (EPM) has important advantages over conventional methods of analysis for organic sulfur in coal: analysis by EPM is done directly, avoiding problems associated with calculating organic sulfur content by difference; organic sulfur contents of individual macerals can be measured in situ in a sample. A major problem with this technique has been finding a suitable sulfur standard. We have recently prepared a petroleum coke and have found it to be a suitable standard.

Background

Matrix effects caused by major differences in composition, structure, and density between organic and inorganic compounds make inorganic minerals (e.g., pyrite) undesirable as standards. Sutherland[1] reported on EPM studies of organic sulfur in coal using pyrite (FeS_2) as a sulfur standard. They used a common data reduction algorithm for matrix (ZAF) corrections, then multiplied by a additional factor to correct for differences in

---

Author L. A. Harris is with the Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830; R. Raymond, Jr. and R. Gooley are with the Geosciences Division, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, 87545. Research sponsored by the Division of Materials Sciences, U.S. Dept. of Energy, under contract W-7405-eng-26 with Union Carbide Corporation and by Office of Basic Energy Sciences, under contract W-7405-ENG-36.

observed x-ray intensities caused by extreme differences in composition between the standard and samples. Initial standardization to derive the correction factor for the particular instrument and conditions used was time consuming, but once achieved, Sutherland suggested analytical time for analysis of organic sulfur could be less than one hour.

Raymond and Gooley[2] reported on organic sulfur contents of various maceral types in coals, determined by EPM using small (75-200 μm dia.), sulfur-bearing carbon beads as a standard. The beads were originally prepared at The Los Alamos Scientific Laboratory for use in nuclear fuel cells. They contain 4.1 wt.% sulfur, are stable under electron bombardment, and eliminate the undesirable matrix effects common to inorganic minerals. The beads were useful in studies involving relative organic sulfur contents of various maceral types, but slight chemical inhomogeneities between beads made development of a better standard desirable.

Organic sulfur contents of coals are typically less than 2 wt.%, and rarely above 4 wt.%. Therefore, an ideal organic sulfur standard for EPM would be a hydrocarbon that contains about 4 wt.% sulfur. We examined a polysulfone resin ($C_{27}H_{22}SO_4$, 9.28 wt.% S) for its potential as a sulfur standard. Though chemically homogeneous, it is sensitive to electron bombardment, as are most organic compounds, and visibly degrades under the electron beam. Avoiding this degradation requires constant sample movement during standardization. We therefore continued our search for a better sulfur standard.

Petroleum Coke: A Good Standard

Petroleum coke, derived from thermal treatment of petroleum pitch, is chemically homogeneous and quite stable during electron bombardment. Petroleum pitch is a thick bituminous substance produced by destructive

distillation of petroleum. Petroleum coke is produced by thermal decomposition of the pitch. Chemical analyses of the pitch before coking gave 92 wt.% carbon, 3.9 wt.% sulfur, 2 wt.% hydrogen, and 0.009 wt.% ash. Petroleum pitch typically contains less than 1% mineral matter.

We converted the petroleum pitch into coke in a batch autoclave by heating it to 300°C for a few hours, raising the temperature to 375°C for five hours, and finally heating at 500°C for 24 hours. Loss of volatile constituents was minimized by constant refluxing during the coking process. Chemical compositions of cokes produced by this process vary little from those of the starting pitches. This process essentially duplicates that of a delayed coking oven.

We prepared a polished section of the product coke; a photomicrograph is shown in Figure 1. Note the lamellar structure of the coke (anisotropic in polarized light) and the large void which is partially filled with a "second phase." The "second phase" is a plastic material that solidified after the coke formed. Its composition is similar to the coke, but the sulfur content may be as much as 1.5 wt.% higher.

To remove the "second phase" we crushed the coke and boiled it overnight in quinoline. The product was then washed thoroughly in alcohol and air dried. The above is a standard method for removing unreacted phases from cokes and does not affect the sulfur in the remaining single phase coke. Analyses made on a Leco sulfur analyzer showed the single phase coke to contain 3.56 ± 0.04 wt.% sulfur.

Using the petroleum coke as its own standard we analyzed 100 random areas of the sample as a homogeneity check, ignoring the lamellar structure of the coke. Using a t-statistics approach, we determined that seven

standardization repeats ensure a standardization value of 3.56± 0.10 wt.% at the 95% confidence level.

Discussion

In this paper we report on petroleum coke that is stable under an electron beam and contains a uniform sulfur content, hence it is a suitable standard for analysis of organic sulfur content of coal. It should be as applicable for analysis of organic sulfur in other fossil fuels.

This standard is available for distribution and may be attained by contacting any of the authors.

References

1. Sutherland, J. K. (1975), Determination of organic sulphur in coal by microprobe, Fuel 54, p. 132.

2. Raymond, R., Jr. and Gooley, R. (1979), A new standard for electron microanalysis of organic sulfur in coal, in Transactions of the 8th International Congress on X-ray Optics and Microanalysis, Science Press, Princeton, NJ.

Fig. 1. Polarized, reflected light microphotograph of the product coke. Note the lamellar structure of the coke, the large pore, and the second phase material partially filling the pore.